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New softness parameters and Hammett's equation†

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The quantitative softness values of a number of substituted Lewis bases (ligands) have been calculated. A scale of softness constant, similar to σ in Hammett's equation has been established. The scale is defined according to the Eq. (1),

$$E_L^{\dagger} = E_{m(eff)}^{\dagger}(BX) - E_{m(eff)}^{\dagger\ (BH)} \quad \ldots (1)$$

The scale is used to analyse the softness values of various mono substituted Lewis bases (BX) in terms of a linear Eq. (2),

$$E_{m(eff)}^{\dagger}(BX) = E_s' + \beta E_L^{\dagger} \quad \ldots (2)$$

where E_s' is the measure of electron richness of the binding site (atom) and β is the measure of polarisability. Other properties such as the type of substituent which replaces hydrogen atom in Lewis base and chemical reactivity of the site are discussed in terms of $E_L^{\dagger}$, β and E_s'. The Eq. (2) can be used for the identification of unknown BX and conversely in the design of electron rich or poor.

In the recent past, we have developed a number of softness parameters, which have been able to explain a number of chemical reactions, particularly the metal-liquid chemistry[1-7]. Attempts are in progress to find more applications of quantitative softness values. In this paper, a new approach, parallel to Hammett's equation, has been developed with the help of softness values.

Materials and Methods

For the evaluation of softness values at particular site in various molecules the following Eq. (4) was used[1],

$$E_{n(eff)}^{\dagger} = IP_n - b^2(IP_n - EA_n) - (X_s(C_s^n)^2/R_s)$$
$$(1 - 1/\varepsilon)[q_s - 2b^2X_s(C_s^n)^2] \quad \ldots (3)$$

$$E_{m(eff)}^{\dagger} = IP_m - a^2(IP_m - EA_m) = (X_r(C_r^m)^2/R_r)$$
$$(1 - 1/\varepsilon)[q_r - 2b^2X_r(C_r^m)^2] \quad \ldots (4)$$

For the solution of the above equations, a programme using BASIC language has been developed which is presented in Appendix I. The a, b, c, atomic number, stability ratio (SR) of atoms etc. were used into a data file for the purpose of calculations. With the help of the programme, we have calculated the softness values of a large number of ions and molecules using DCM Olympia mini computer. The softness values have been used to develop a new parameter, known as softness constant $E_L^{\dagger}$.

Results and Discussion

Hammett[8] used benzoic acid as a standard aromatic and measured the change in its acid strength by the replacement of one hydrogen atom by a substituent X in *meta* or *para* position. He designated the difference in strength induced by the substituent X by σ and defined it by the following Eq. (5).

$$\sigma = \log K_i^x - \log K_i^0 \quad \ldots (5)$$

Table 1—Softness constants of various substituents

Substituent	$E_L^{\dagger}$
NO_2	+0.56
$COCl_2$	+0.40
F	+0.34
Cl	+0.24
OH	+0.22
NCS	+0.21
Br	+0.17
CN	+0.16
NH_2	+0.07
I	+0.06
$NHCH_3$	+0.03
CH_3	−0.04
C_2H_5	−0.07
H	0.00

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Table 2—Effective softness values of monosubstituted Lewis bases

Subs. (X)	E_m^+ of A	E_m^+ of B	E_m^+ of C	E_m^+ of D	E_m^+ of E
NO_2	−10.20	−10.71	−10.81	−10.67	−11.12
$COCl_2$	−10.36	−10.81	−10.94	−10.67	−11.12
F	−10.42	−10.87	−10.96	−10.81	−11.12
Cl	−10.52	−10.95	−11.06	−10.87	−11.25
OH	−10.54	−10.96	−11.10	−10.88	−11.26
NCS	−10.55	−10.96	−11.13	−10.89	−11.26
Br	−10.59	−10.99	−11.13	−10.91	−11.28
CN	−10.60	−11.00	−11.15	−10.92	−11.28
NH_2	−10.69	−11.06	−11.24	−10.97	−11.31
I	−10.70	−11.08	−11.24	−10.98	−11.32
$NHCH_3$	−10.73	−11.10	−11.31	−11.01	−11.33
CH_3	−10.80	−11.15	−11.36	−11.05	−11.36
C_2H_5	−10.83	−11.17	−11.40	−11.08	−11.42

A = pyridine derivatives, B = Ethylenediamine derivatives, C = Isothiazole derivatives, D = Morpholine derivatives and E = Bipyridyl derivatives.

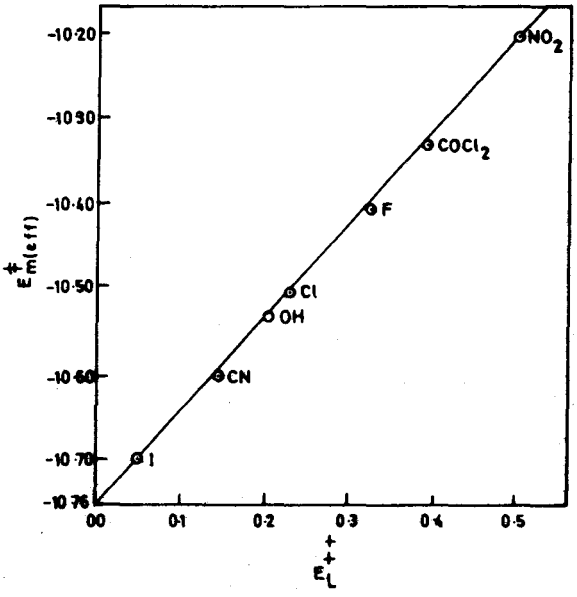

Fig. 1—Plot of $E_{m\ (eff.)}^+$ of pyridine derivatives versus softness constants E_L^+

where K_i^x and K_i^0 are ionisation constants of substituted and unsubstituted benzoic acids respectively. The plot of log K_i^x against σ produced non-parallel linear plots which are represented by the following Eq. (6)

$$\log K_i^x = \log K_i^0 + \sigma\rho \qquad \ldots (6)$$

A new parameter, softness constant E_L^+ similar to σ in Hammett's equation has been developed. This parameter may be defined as the difference of softness of monosubstituted base with the softness of unsubstituted base. For instance, when one hydrogen atom is replaced by an electron attracting group or electron repelling group in pyridine, its softness value changes. The change in the softness value depends upon the nature of the substituted group X.

Table 3—E_s' and β values of various Lewis bases

Lewis base	E_s'	β
Pyridine	−10.76	1.00
Ethylenediamine	−11.12	0.73
Isothiazole	−11.29	0.86
Morpholine	−11.01	0.59
Bipyridyl	−11.34	0.39

Pyridine has been chosen as standard for the development of the new parameter E_L^+. A number of monosubstituted derivatives of pyridine have been taken and the softness at nitrogen has been calculated. The results are presented in Table 1. The values have been substituted in the following equation which is similar to Hammett's Eq. (5),

$$E_L^+ = E_m^+(C_5H_4NX) - E_m^+(C_5H_5N)$$

where E_L^+ is the softness constant, $E_m^+(C_5H_5N)$ and $E_m^+(C_5H_4NX)$ are the softness values of pyridine and its monosubstituted derivatives at ring nitrogen respectively. The softness constant is the change in the softness value of pyridine, measured in eV, induced by the replacement of one hydrogen atom by an electron attracting or electron repelling group or atom. From the above discussion, it follows that the softness constant of hydrogen is zero.

From Table 1, it is clear that strong electron at-

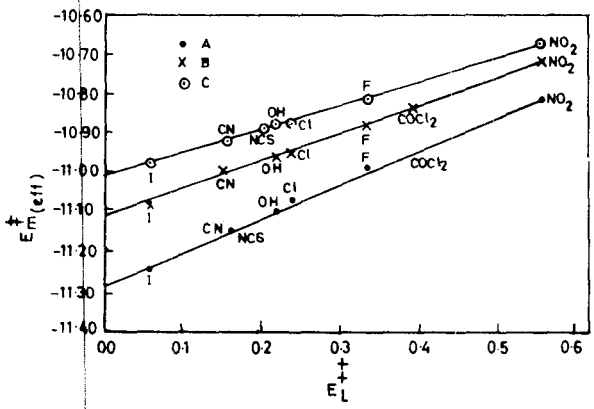

Fig. 2—Plots of $E^{\ddagger}_{m(eff)}$ of isothiazol derivatives (A), ethylenediamine derivatives (B) and morpholine derivatives (C) versus $E^{\ddagger}_{L}$

tracting groups such as NO_2, F, Cl, etc. have high positive value of $E^{\ddagger}_{L}$ whereas electron repelling groups like CH_3, C_2H_5 etc. have negative values.

On plotting the softness values of various monosubstituted Lewis bases against $E^{\ddagger}_{L}$ values considering pyridine as standard, non-parallel linear plots are obtained (Fig. 1). These plots can be represented by the following equation which is similar to Hammett's Eq. (6),

$$E^{\ddagger}_{m}(BX) = E'_{s} + \beta E^{\ddagger}_{L}$$

where $E^{\ddagger}_{m}(BX)$ is the softness of monosubstituted Lewis base and E'_{s} and β are the two new parameters. These parameters characterise the site of bonding of Lewis base. Therefore, $E^{\ddagger}_{m}(BX)$ is defined by softness constant and two site constants. The site constant E'_{s} gives the measure of the electron richness of the binding site of Lewis base and is actually the value of softness of Lewis base, when there is no substituent (H is the substituent for which $E^{\ddagger}_{L}$ is zero). β is the slope of the line $E^{\ddagger}_{m}(BX)$ versus $E^{\ddagger}_{L}$ and is dimensionless. It is a measure of the polarisability of site and the efficiency of transmission of electronic influence from X to the binding site.

Since the softness constant together with the site constants E'_{s} and β defines the softness of monosubstituted Lewis base, the effect of monosubstitution by an electron attracting or electron repelling group in Lewis base for a particular site can be calculated in terms of softness constant. The softness constants calculated for pyridine and its monosubstituted derivatives are presented in Table 2. The values E'_{s} and β may be estimated for a particular site, provided atleast two values of $E^{\ddagger}_{m}(BX)$ for a series are given and the corresponding values of $E^{\ddagger}_{L}$ are known. The $E^{\ddagger}_{m}(BX)$ of other bases like ethylenediamine, isothiazole, morpholine and bipyridyl and their derivatives have also been evaluated and the results are presented in Table 3. The principle is therefore, applicable not only to pyridine, but to other bases as well.

Table 4—E'_{s} values of bases having two bonding sites

Base	E'_{s} of site N	E'_{s} of site O/S/Se
Isothiazole	−11.29	−8.19
Morpholine	−11.01	−10.37
Thiocyanate	−12.56	−8.13
Selenocyanate	−12.51	−7.67

Predictive use of softness constant ($E^{\ddagger}_{L}$)

Plots of $E^{\ddagger}_{m}(BX)$ versus softness constant $E^{\ddagger}_{L}$ give linear relationship similar to the plots of aromatic rates against Hammett's σ constant. Figure 2 shows the plots of softness of various monosubstituted Lewis bases versus softness constant $E^{\ddagger}_{L}$. It is evident from the plots that the substituent X has great influence on the electron richness and polarisability of the binding atom of the Lewis base.

The electron rich sites for which the quantitative softness value will be more negative, can be predicted by the softness constant $E^{\ddagger}_{L}$ of the substituents. The Lewis base with substituent X, having more negative value of $E^{\ddagger}_{L}$, will also have more negative value of softness of binding atom, for example substituent, C_2H_5, has more negative value of $E^{\ddagger}_{L}$ than CH_3 (Table 1), hence, Lewis base with substituent C_2H_5 will have more negative value of softness. The sites having more negative values of softness will favour electrophilic attack on binding site. Similarly electron poor site will prefer to nucleophilic attack.

Characteristics of site constants (E'_{s} and β)

There are a number of ligands which have more than one site of bonding and it becomes difficult, to ascertain the actual bonding site, e.g. thiocyanate, selenocyanate, isothiazole and morpholine etc. have more than one site through which they can react. The two site constants E'_{s} and β are important and can define the site of bonding to a reasonable accuracy. The site with more negative value of the softness and E'_{s} will be the possible site of bonding, e.g. morpholine, isothiazole, thiocyanate, selenocyanate etc. have two bonding sites, one being at nitrogen and other at either sulphur or oxygen. Table 4 shows that the softness constant E'_{s} has more negative value at nitrogen end which is the actual site of bonding.

The softness constant $E^{\ddagger}_{L}$ is siffuciently fundamental to allow the prediction of softness of Lewis base or ligand. Much information can be contained in only one constant. The softness constant can

serve as a reasonable guide to cover electron donor capacities of ligands.

APPENDIX–I

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10 INPUT "PLEASE TYPE ATOMIC NO.
   WHOSE SOFTNESS IS TO BE CALCU-
   LATED": AN
20 Z = 1
30 OPEN "A", #3, "A: S3.DAT"
40 OPEN "I", #1, "A: S1.DAT"
50 OPEN "R", #2, "A: S2", 9
60 INPUT #1, ATNO, A,B,C,SR MS,NL,QO,X
70 Z = Z + 1
80 IF AN < > ATNO THEN GOTO 60
90 INPUT "PLEASE TYPE VALUE OF R"; R
100 INPUT "PLEASE TYPE VALUE OF
   EPSILON"; EP
110 INPUT "TYPE FORMULA OF MOLE-
   CULE"; F$
120 INPUT "PLEASE TYPE THE VALUE OF
   Q"; CUE: CUE1-CUE
130 N = LEN(F$)-2: SUM = 1: CA = 0
140 FOR I = 1 TO N STEP 5
150 AM = VAL(MID$(F$, I, 3))
160 OC = VAL(MID$(F$, I + 3, 2))
170 CA = CA + OC
180 FIELD #2, 3 AS AT$, 6 AS SRA$
190 GET #2, AM
200 SRO = CVS(SRA$)
210 SUM = SUM* SRO ∧ OC
220 NEXT I
230 KM$ = RIGHT$ (F$, 2)
240 PRInt "SUM"; SUM
250 PRINT "NO OF ATOMS"; CA
260 SRM = SUM ∧ (1/CA)
270 PRINT "STABILITY RATIO = ...."; SRM
280 PC = (SRM-SR)/(2.08*SQR(SR))
290 IF KM$ = "MM" THEN CUE = CUE + PC
300 IF KM$ = "L" THEN XR = PC-(PC-
   1)*SQR(.75): GOTO 320
310 XR = CUE-(CUE-1)* SQR (.75)
320 PRINT "XR = ....."; XR
330 PRINT "PARTIAL CHARGE = "; PC
340 IF KM$ = " THEN Q = AN-PC ELSE
   Q = AN-(CUE1-2)-PC
350 PRINT "Q = ....."; Q
360 EA = A + B*Q + C*(Q ∧ 2)
370 PRINT "ELECTRON AFFINITY = ...."; EA
380 IP = A + B*(Q-1) + C*(Q-1) ∧ 2
390 PRINT "IONISATION POTENTIAL = ..."; IP
400 KM$ = RIGHT$ (F$.2)
410 IF KM$ = "L" THEN 01 = IP-3* (IP-EA)/4
   ELSE 01 = IP-(IP-EA)/4
420 IF KM$ = "L" THEN 02 = (XR/R)* (1-1/EP)*
   (PC + XR/2)* 15.488: GOTO 450
430 IF KM$ = "MM" THEN 02 = (XR/R)* (1-1/
   EP)* (CUE-XR/2)* 14.387; GOTO 450
440 02 = (XR/R)* (1-1/EP)* (CUE1-XR/2)*
   14.387
450 PRINT "ORBITAL ENERGY OE = "; 01
460 PRINT "DESOLVATION ENERGY DE =
   ..."; 02
470 EN = 02-01
480 PRINT "SOFTNESS OF THE METAL
   ION = ....."; EN
490 INPUT "DO YOU WANT TO STORE
   ABOVE RESULT. (Y/N) ...?" ANS$
500 IF ANS$ = "N" OR ANS$ = "n" THEN 520
510 WRITE #3, F1$, SUM1, CA1, SRM1, XR1,
   PC1, Q1, EA1, IP1, 011, 022, EN1
520 CLOSE #1, #2, #3: END
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